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(54) Title: SACRIFICIAL MOLDING

(57) Abstract

This invention relates to a water soluble core material for injection molding.

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SACRIFICIAL MOLDING

Field of the Invention

According to the present invention, there is provided a core material excellent in heat resistance and fluidity, which is to be used for injection molding, especially for the production of a fine injection molded product, e.g. a fastener member.

Background of the Invention

U.S. Pat. Nos. 4,216,257; 4,290,174 and 5,040,275 disclose engaged face fastener members composed of a base portion, stem portion, and mushroom type head portion, and processes for the production thereof. However, the processes for the production of these members are complicated and have not been suitably used for the production of an engaged face fastener member having a fine pitch or a complicated shape of base portion or head portion.

Thus, there may be conceived a process for the production of an engaged face fastener member by injection molding by utilization of a water soluble core material capable of being broken away. That is, if the stem portion alone is produced by use of such a water soluble core material, and the base portion and head portion are produced by combination of permanent molds, the aforesaid production process for an engaged face fastener is applicable also to the aforesaid engaged face fastener having a fine pitch and complicated base shape or head shape.

In this connection, there have been known the following materials as general water soluble material.

(1) Carboxyl group-containing acrylic high molecular weight materials as water soluble core material to be used in a mold for injection molding or the like, which are disclosed in Japanese Unexamined Patent Publication (Kokai) No. 155212 and EP 0314156.

(2) Amino group-containing high molecular weight materials soluble in an acid solvent or an alkali solvent, which are disclosed in U. S. Pat. Nos. 4,990,146 and 4,870,148.

(3) Material composed of inorganic salts and inorganic fibers, as water soluble core material to be used for die casting, which is disclosed in Japanese Unexamined Patent Publication (Kokai) No. 51-50218.

(4) Material consisting of water soluble powder and ceramics powder, to be used in a mold for injection molding and the like, which is disclosed in Japanese Unexamined Patent Publication (Kokai) No. 62-255104.

(5) Material comprising a carboxyl group-containing acrylic high molecular weight material with an added filler, as a water soluble core material to be used in a mold for injection molding and the like, which is disclosed in Japanese Unexamined Patent Publication No. 1-198609.

However, these materials are poor in heat resistance, fluidity, and water solubility, and have generally been insufficient in such properties as a core material for injection molding, especially as a core material for the production of fine injection molded products, e.g. the aforesaid engaged face fastener member.

The purpose of the present invention is to provide a core material excellent in heat resistance, fluidity, and water solubility, which is to be used for injection molding, especially for the production of fine injection molded products, e.g. an engaged face fastener member.

Description of the Invention

The present invention relates to a water soluble core material to be used in a mold for injection molding, said core material containing a water soluble high molecular weight compound having a hydroxyl group.

The reasons why the essential component of the core material is limited to a hydroxyl group-containing high molecular weight compound, in the present invention, reside in the following.

(a) A hydroxyl group-containing high molecular weight compound is excellent in water solubility, and the core material consisting essentially of such a compound is easily dissolved in water or hot water.

(b) Owing to the hydrogen bond of the high molecular weight compound, the core material consisting essentially of this high molecular weight compound is excellent in thermal stability, and even at a melting temperature of an injection molded resin at the time of molding of an injection molded product, e.g. at a temperature exceeding 200°C, the period of time during which a high temperature is maintained is so short that.it is possible to retain a pertinent shape. In particular, in an injection molded product of a fine shape, since the melt temperature of the injection molded product is made higher in order to enhance the fluidity thereof, the core material having hydroxyl groups of the present invention is favorable as a core material used for the above purpose.

(c) On the other hand, even-when the core material itself is injection molded, since the hydroxyl groups are mutually reacted with lower reactivity than other functional groups, e.g. carboxyl groups, the injection temperature can be elevated, and as a result, excellent fluidity and thermal stability can be obtained.

(d) In addition, since water or hot water can be used as a solubilizing agent, a core material can be produced safely and inexpensively.

Concrete examples of the aforesaid hydroxyl group containing water soluble high molecular weight compound include polyvinyl alcohol (PVA), hydroxypropyl cellulose, alkyl cellulose, polyvinyl butyral, polyvinyl formal, and the like.

Next, there will be explained about the proportional amount of hydroxyl group content. In the present invention, the proportional amount of hydroxyl groups, e.g. saponification degree is favorably within the range between 70 and 95 mol-%. The reason therefor is that when the hydroxyl group concentration is less than 70 mol-%, it is difficult to obtain excellent water solubility, and on the contrary, when the hydroxyl group concentration exceeds 95 mol-%, the hydroxyl groups are mutually reacted at a temperature of about 240°C, and dehydration and crosslinking reaction are caused, which often result in noticeable lowering of water solubility.

In addition, as the functional group(s) contained in the water soluble high molecular weight compound in the present invention, although hydroxyl groups are preferable, the high molecular weight compound may contain other functional groups, e.g. carboxyl group or amino group together with hydroxyl groups.

The Tg value of the core material of the present invention is within the range preferably between 40 and 100°C. When the Tg value is less than 40°C, the core material becomes poor in heat resistance, and it becomes difficult for the core material to be used in a mold for injection molding. on the other hand, when the Tg value exceeds 100°C, it becomes difficult for the core itself to be injection molded, and the water solubility of the core material becomes lowered, resulting in difficulty of the use thereof for an injection molded product of a fine shape. In addition, the above Tg value can be determined by a differential scanning calorimeter (DSC).

In addition, the melt index (MI) of the core material of the present invention is preferably within the range between 0.1 and 50 (determined according to ASTM D-1238, at 210°C, under loading of 2160g). When MI is less than 0.1, the core material becomes poor in fluidity, and it becomes difficult to use it especially as a core material for an injection molded product of a fine shape. On the other hand, when MI exceeds 50, the average molecular weight of the core material becomes comparatively lowered and poor in heat resistance.

The core material of the present invention may optionally contain an oxazoline compound, in addition to the aforesaid water soluble high molecular weight compound. The oxazoline compound is defined as a molecular material containing an oxazoline skeleton in a molecule, and as the oxazoline compound, there may be used e.g. 2-vinyl-2-oxazoline, 5-methyl-2-vinyl-2-oxazoline, 4,4-dimethyl-2-vinyl-2-oxazoline, 4,4-dimethyl-2-vinyl-5,6-dihydro-4 H-1,3-oxazine, 4,4,6-trimethyl-2-vinyl-5,6-dihydro-4 H-1,3-oxazine or a polymeric product thereof, e.g. poly(2-ethyl-2-oxazoline) and the like.

The reason why it is favorable to herein add an oxazoline compound is that the fluidity and water solubility of the core resin can be improved, retaining the heat resistance of the core resin. The amount of the added oxazoline compound is favorably within the range between 5 and 3-0 parts by

weight based on 100 parts by weight of the aforesaid hydroxyl group-containing water soluble high molecular weight compound. When the amount of the added oxazoline compound is less than 5 parts by weight, there cannot be obtained a noticeable improving effect due to the addition of the oxazoline compound, and on the other hand, when this amount exceeds 30 parts by weight, there is a risk of lowering the heat resistance of the core material.

Next, the core material of the present invention may contain a polyhydric alcohol compound. A polyhydric alcohol compound is favorable, for the reason that the fluidity of the core resin is noticeably improved by addition of a small amount of the polyhydric alcohol compound, and that since the polyhydric alcohol compound has a plurality of hydroxyl groups in a molecule, there are hydrogen bonds in a molecule, and therefore, the boiling point of the alcohol compound is comparatively high and the alcohol compound does not often cause the troubles such as foaming and bleeding. In addition, a polyhydric alcohol compound is preferable also in the point that it improves the dispersibility of fillers of inorganic matter or metallic oxide, when the core material of the present invention contains these fillers.

The polyhydric alcohol compound herein referred to is defined as a compound having 2 or more hydroxyl groups in a molecule, and as the polyhydric alcohol compound, there can be used e.g. glycerine, ethylene glycol, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, hexamethylene glycol, propylene glycol, 2,3-butanediol, 1,3-butanediol, diethylene glycol, triethylene glycol, lecithin, and the like. The amount of the added polyhydric alcohol compound is favorably within the range between 0.1 and 10 parts by weight based on 100 parts by weight of the hydroxyl group-containing high molecular weight compound. When the amount of the added polyhydric alcohol compound is less than 0.1 part by weight, there is obtained only poor improving effect due to the addition of the polyhydric alcohol compound, and on the other hand, when the amount exceeds 10 parts by weight, there is a fear that the Tg value of the aforesaid water soluble high molecular weight compound, and in its turn, the Tg value of the core material should extremely be lowered.

The core material of the present invention may contain a filler, and owing thereto, the heat resistance of the core material is improved, and the

mechanical strength thereof is improved, an extending effect (reduction of production cost) results, the fluidity of the core material is improved, when the material is injection molded, the solubility of the core material in water is increased, the surface of the injection mol ded product becomes flat and smooth, and the storage stability of the core material is improved.

As the aforesaid filler, there may be used talc, glass beads, hollow glass beads, silica particles, alumina oxide, calcium carbonate, titanium oxide, magnesium oxide, zinc oxide, zirconium oxide, alumino siliocate, mica, barium sulfate, calcium phosphate, kaolin, zeolite, iron, titanium, nickel, copper, magnesium, tin, lead, zinc, metallic salts, crosslinked silicon resin, and the like.

The amount of the aforesaid filler to be added is favorably within the range between 1 and 200 parts by weight based on 100 parts by weight of the hydroxyl group-containing water soluble high molecular weight compound. When this amount is less than 1 part by weight, the improving effect caused by the addition of the filler is poor. When this amount exceeds 200 parts by weight, the moldability of the core becomes poor, and there is a fear that an injection molding machine should be abraded.

The aforesaid filler has an average particle diameter, measured by an image processing device, preferably ranging from 0.1 to 600 μm, particularly preferably ranging from 1 to 200 μm. When the particle diameter is less than 0.1 μm, there can be obtained only a poor improving effect due to the addition of the filler, and it is difficult to disperse the filler into the aforesaid high molecular weight compound. When the particle diameter of the filler exceeds 600 μm, the injection molded product becomes poor in surface smoothness. In addition, even when the filler is to be applied to an injection molded product of a fine shape, it is possible to optionally adjust the particle diameter by pulverization of the filler, in the case where the filler is to be dispersed int o a high molecular weight compound by use of a screw or the like, so long as the original particle diameter of the filler is 600 μm or less, and therefore, the filler having a particle diameter of 600 μm or less can be used in the present invention. In addition, when the particle diameter of the filler is within the range between 1 and 200 μm, the filler has the advantages that there is little fear that the filler should abrade the injection molding

machine used, that it can be easily separated from the high molecular weight compound, and that the waste liquid can easily be disposed, so that the filler can easily be applied to an injection molding of a fine shape.

The density of the aforesaid filler is favorably 1.05 or more or 0.95 or less. The reason therefor is that when the density is 1.05 or more, the particles thereof are likely to be settled when dissolving the water soluble core, and it is possible to dissolve the water soluble core more easily by use of a centrifugal separator. In addition, more preferable density of the filler is 1.3 or more, because separation and recovery of the particles of the filler from the water soluble core become easier. On the other hand, the reason why the density of the filler is preferably 0.95 or less is that since the particles of the filler float on the water surface in the case of dissolving the water soluble core, separation and reutilization of the particles are very easy.

The shape of the aforesaid filler particles is desirably a spherical one having a uniform particle size distribution. The reason therefor is that the filling rate of the filler into the resin can be made very noticeably higher as compared with the case where an indeterminate filler is used, and that even if the filler is added in a large amount, it gives little influence to the fluidity of the core resin when injection molding the core resin, so long as the filler is composed of particles of a uniform spherical shape. In addition, owing to the high mechanical strength of the filler, the filler can be reutilized, and the production cost thereof can be lowered. Further, since the filler is easily arranged on the core surface, the surface smoothness and reproducibility of the produced injection molded product become higher.

In order to enhance the compatibility of the above filler with the core material, it is favorable to surface-treat the filler with a silane coupling agent and/or a titanium coupling agent.

The core material of the present invention may contain a pigment or a dye. In a step of dissolving the core material in water, since the concentration of the core material in water exhibits a strong influence to the dissolving rate of the core material, handling of the aqueous solution becomes important. Accordingly, it becomes possible to very simply conduct such handling by viewing or the like by utilization of a pigment or dye which is dissolved out together with the core. In addition, by use of a pigment or dye

with a color different from that of the injection molded product, it becomes possible to very easily judge the insufficiency of the solubility of the core material by viewing or the like. On the other hand, by use of a pigment or dye having the same color as the injection molded product, even when the core material is somewhat adhered to the injection molded product in such an extent as may not impair the function of the injection molded product, there is little fear that the external appearance of the injection molded product should be injured.

The kind of the aforesaid pigment or dye is not particularly limited. As the pigment or dye, there may be used organic pigments or organic dyes, e.g. azo dyes, nitroso dyes, anthraquinone type dyes, indigo type dyes, sulfur dyes, basic dyes, acid dyes, thiazole type dyes, naphthol dyes and the like.

The amount of the aforesaid pigment or dye to be added can be determined, judged from the chromaticity, color value, chroma and the like. In concrete, the amount of the pigment or dye to be added is favorably within the range between 0.01 and 5 parts by weight based on 100 parts by weight of the hydroxyl group-containing water soluble high molecular weight compound. When this amount is less than 0.01 part by weight, there is generally obtained only a poor coloring effect. On the other hand, when this amount exceeds 5 parts by weight, handling of the aqueous solution produced in the step of dissolving the core material in water becomes difficult, on the contrary.

The core of the present invention may contain carbon black. Owing to the contained carbon black, there can be improved the heat resistance and reinforcing effect of the core material. Owing to the comparatively small particle diameter of carbon black, the surface smoothness of the injection molded product is improved. In addition, since carbon black is excellent in hiding power, the core material can be turned black by addition of a small amount of carbon black. On the other hand, if the color of the injection molded product is made blackish one, even in the case where the core material is somewhat adhered to the injection molded product in such an extent as may not impair the function of the injection molded product, there is little fear that the external appearance of the injection molded product should be marred by the core material. It becomes possible to effect handling

of the aqueous solution by viewing or the like, with the carbon black flown out together with the core. In addition, since carbon black is inexpensive, it produces also an extending effect.

The kind of carbon black is not particularly limited. As concrete examples of carbon black, there may be used channel black, thermal black, furnace black, and the like.

The amount of carbon black to be added can be set, judging from the degree of blackness or the like. In concrete, this amount is favorably within the range between 0.05 and 20 parts by weight based on 100 parts by weight of the hydroxyl group containing water soluble high molecular weight compound. When this amount is less than 0.05 part by weight, the added carbon black generally produces only a poor improving effect. On the other hand, when this amount exceeds 20 parts by weight, handling of the aqueous solution produced in the step of dissolving the core material in water becomes difficult, on the contrary.

In the following, the present invention will be explained in more detail with reference to working examples.

<u>Examples 1 to 8 and Comparative Example 1</u>

Polyvinyl alcohols produced by Japan Synthetic Chemistry Co., Ltd. or acrylic water soluble resins produced by Berrant Inc., which are set forth in Table 1, were, respectively, dried for 24 hours or longer by use of a hot-air dryer, the temperature of which had been controlled at 50°C, whereafter cores were molded, at a temperature of 210°C or 225°C, by use of a core type 6 produced by Sumitomo 3M Co., Ltd., by a molding machine of PS-40 type manufactured by Nissei Resin Industries Co., Ltd. Subsequently, by use of the thus produced cores, there were prepared standard face fasteners made of M 4745 polypropylene produced by Asahi Kasei K.K. by use of the aforesaid molding machine of PS-40 type manufactured by Nissei Resin Industries Inc., and the thus prepared face fasteners were subjected to the following evaluations. The results are set forth in Table 1.

(1) Measurement of the Tg values of the core materials:
By use of "DSC-2C" manufactured by Perkin Elmer Inc., the temperature of the core materials was elevated from -60°C to

300°C at a rate of 10°C/min, and the temperatures at which specific heats of the cores were changed, respectively, were determined in a dynamic mode, and the thus determined temperatures were represented as Tg values, respectively.

(2) Measurement of MI values of the core materials:

MI values of the core materials were determined, respectively, by use of a melt indexer, "S-101" manufactured by Toyo Seiki Inc. according to ASTM D-1238 (at 210°C, under a load of 2160g).

(3) Measurement of core packing rates (actual weight of core resin/theoretical weight of core resin):

The proportion of the weight of each core material prepared by actually injection molding the core resin at a temperature of 210°C or 225°C, based on the theoretical core resin weight obtained from the volume of each core mold was represented as a core packing rate.

(4) Evaluation of solubility:

The prepared core materials were dipped in water or hot-water of 23°C or 70°C for 24 hours, whereafter the solubility of each core material was judged by viewing according to the following criterion.

OK: completely dissolved

FAIR: almost completely dissolved

NG: partially remained

(5) Evaluation of the external appearance of engaged face fastener:

Each of the produced engaged face fasteners was judged as for external appearance according to the following criterion.

OK: no problem

NG: partially objectionable

PVA, etc. (*1)	Examples								Comparative Example
	1	2	3	4	5	6	7	8	1
	KP06	KL05	KM11	GL03	GL05	GM14	GH23	NL05	GBC1330TE
Saponification Degree	71	80	78	87	88	90	87	90<	-
Tg/°C	57.0	73.4	75.0	69.4	68.0	74.5	72.0	80	-
MI	4.0	3.3	2.6	4.5	3.1	0.3	0.1	2.0	8.2
Packing Rate									
210°C	100	100	95	100	100	80	65	100	100
225°C	100	100	100	100	100	100	100	100	100
Solubility									
25°C	OK	OK	OK	OK	OK	OK	OK	NG	NG
70°C	OK	OK	OK	OK	OK	OK	OK	OK	FAIR
External Appearance	OK	OK	OK	OK	OK	OK	OK	OK	NG

*I) KPO6, KLO5, KM11, GLO3, GLO5, GM14, GH23, and NLO5 are trade names of polyvinyl alcohols produced by Japan Synthetic Chemistry Co., Ltd.

GBC 1330TE is a trade name of an acrylic water soluble - resin produced by Berrant Inc.

Examples 9 to 13 and Comparative Example 2

As set forth in Table 2, polyvinyl alcohols produced by Japan Synthetic Chemistry Co., Ltd. were, respectively, dried for 24 hours by use of a hot-air dryer, the temperature of which had been controlled at 50°C, following which a polyhydric alcohol, oxazoline compound, carbon black, and filler were added to each of the polyvinyl alcohols and sufficiently mixed, to obtain core materials. Subsequently, standard face fasteners were produced in the same manner as in Example 1, and subjected to the same evaluations as in Example 1. The results are set forth in Table 2. The numeral affixed to each of the component signs represents a formulated proportional amount (wt-%) of the component.

Core Material (*2)	Examples					Comparative Example
	9	10	11	12	13	
	GL03/75 GRI/3 AO-5032/22	XL05/85 GRI/0.1 PEOX/15	GL05/79 C.B./1 talc/20	GL03/99 ML3050/1	GL03/40 SO-C5/60	GL03/80 GRI/17.5 PEOX/2 talc/0.5
Tg/°C	54	68	67	69	69	32
MI	8.4	3.8	3.6	3.7	4.5	60
Saponification Degree	87	80	88	87	87	87
Packing Rate						
210°C	100	100	100	100	100	103
225°C	100	100	100	100	100	104
Solubility						
25°C	OK	OK	OK	OK	OK	OK
70°C	OK	OK	OK	OK	OK	OK
External Appearance	OK	OK	OK	OK	OK	NG

*2) GRI = glycerine, produced by Wako Pure Chemical Industries, Ltd.

PEOX = trade mark of polyethylene oxazoline produced by Dow Chemical Inc.

C.B. = carbon black produced by Asahi Carbon Co. Ltd., "Asahi Carbon Black" (trade mark). Average particle diameter (determined by an electron microscope or an image-processing device; the same as hereafter): 80 WM.

AO-502 = trade name of "Admafine" (trade mark), alumina powder of spherical particles produced by Admatechs Co., Ltd. Average particle diameter: 0.1 to 0.7 gm, density: 3.6

talc = produced by Japan Talc Co., Ltd., scale-like, particle size: 7.0 Vm, density: 2.7

ML3050 = trade name of "Macrolite" (trade mark), spherical particles of alumina silicate produced by 3 M Co., U. S. A., Average particle diameter: 300 to 600 μm, Density: 1.05

SO-C65 = trade name of "Admafine" (trade mark), silica powder of spherical particles produced by Admatechs Inc., Average particle diameter: 1.5 to 2μ, Density: 2.21

Examples 14 to 17

As set forth in Table 3, polyvinyl alcohols produced by Japan Synthetic Chemistry Co., Ltd. were dried for 24 hours by use of a hot-air dryer which had been temperature controlled to 50°C, following which fillers with varied kinds of filler, particle diameters, and densities were, respectively, added to the polyvinyl alcohols and sufficiently mixed, so as to prepare core materials. Subsequently, standard face fasteners are produced in the same manner as in Example 1, and subjected to the same evaluations as in Example 1. The results are set forth in Table 3.

	Examples			
	14	15	16	17
Filler	GL03/80	GL03/80	GL03/80	GL03/80
/PHR	20	20	20	20
Kinds (*3)	GB731	SO-C 2	ML3050	C-15/250
Average Particle Diameter (μm)	30	0.5	300-600	66
Density	2.5	2.2	1.05	0.15
Tg/°C	69	69	68	68
MI	6.1	5.3	2.8	1.9
Packing Rate				
210°C	100	100	100	100
225°C	100	100	100	100
Solubility				
25°C	OK	OK	OK	OK
70°C	OK	OK	OK	OK
External Appearance	OK	OK	OK	OK

*3) GB731 = Trade name of the glass beads produced by Toshiba Ballotiene Inc.

SO-C2 = trade name of "Admafine" (trade mark), silica powder of spherical particles produced by Admatechs Co., Ltd.

C15/250 = trade name of "Scotch Light Glass Bulbs" (trade mark), glass balloons produced by 3M Co., U.S.A.

WHAT IS CLAIMED IS:

1. In a core material used in a mold for injection molding, a water soluble core material for injection molding, which comprises a water soluble high molecular weight compound having hydroxyl groups.

2. A water soluble core material for injection molding according to Claim 1, wherein said water soluble high molecular weight compound has a saponification degree ranging from 70 to 95 mol-%.

3. A water soluble core material for injection molding according to Claim 1, wherein the Tg value of said core material is within the range between 40 and 100°C.

4. A water soluble core material for injection molding according to Claim 1, wherein the melt index of said core material is within the range between 0.1 and 50 (according to ASTM D-1238, 210°C, under loading of 2160g).

5. A water soluble core material for injection molding according to Claim 1, wherein said core material contains an oxazoline compound.

6. A water soluble core material for injection molding according to Claim 1, wherein said core material contains a polyhydric alcohol compound in a proportional amount ranging from 0.1 to 5 parts by weight based on 100 parts by weight of said water soluble high molecular weight compound.

7. A water soluble core material for injection molding according to Claim 1, wherein said core material contains a filler.

8. A water soluble core material for injection molding according to Claim 7, wherein said core material contains a filler in a proportional amount ranging from 1 to 200 parts by weight based on 100 parts by weight of said water soluble high molecular weight compound.

9. A water soluble core material for injection molding according to Claim 7, wherein the particle diameter of said filler is within the range between 0.1 and 200 μm.

10. A water soluble core material for injection molding according to Claim 7, wherein the density of said filler is 1.05 or more.

11. A water soluble core material for injection molding according to Claim 7, wherein the density of said filler is 0.95 or less.

12. A water soluble core material for injection molding according to any of Claim 1, wherein said core material contains a pigment or dye.

13. A water soluble core material for injection molding according to any of Claim 1, wherein said-core material contains a carbon black.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C45/44 B29C33/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 184 874 (OLSON) 9 February 1993 see column 4, line 33 - line 38 ---	1,7
X	US,A,4 877 569 (URBISH) 31 October 1989 see claims 1,2 ---	1
X	FR,A,2 672 536 (MAURO) 14 August 1992 see page 3, line 30 - page 4, line 13 ---	1
P,X	WO,A,93 22120 (MINNESOTA MINING AND MANUFACTURING CO.) 11 November 1993 see page 9, line 27 - line 31 --- -/--	1,7

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
14 December 1994	02.01.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	BOLLEN, J

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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